Mini-Review

Mini-Review on the Redox Additives in Aqueous Electrolyte for High Performance Supercapacitors

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ABSTRACT: Supercapacitors, also known as electrochemical capacitors, are attracting much research attention owing to their high power density, long-term cycling stability, as well as exceptional safety compared with rechargeable batteries, although the globally accepted quantitative benchmarks on the power density, cycling stability, and safety are yet to be established. However, it should be noted that the supercapacitors generally exhibit low energy density, which cannot satisfy the demands where both high energy density and power density are needed. To date, various methods have been employed to improve the electrochemical performances of supercapacitors. Among them, introducing redox additives (or redox mediators) into conventional aqueous electrolyte is regarded as one of the most promising strategies. The redox additives in aqueous electrolyte are widely demonstrated to be able to increase the charge storage capability via redox transformation and thus enhance the electrochemical performances. Herein, we present a brief review on the classification, state-of-the-art progress, challenges, and perspectives of the redox additives in aqueous electrolyte for high performance supercapacitors.

Redox species
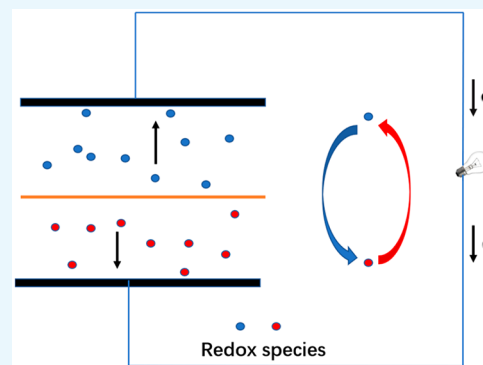
INTRODUCTION

Growing research attention has been paid to the various kinds of energy storage systems in recent years owing to the concerns of the depletion of fossil fuel reserves and associated burgeoning demand for the renewable energies such as solar energy and wind energy. Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have been regarded as one of the most promising candidates for energy storage with fantastic properties of high power density, long-term cycling stability, as well as exceptional safety,[1] although the globally accepted quantitative benchmarks on the power density, cycling stability, and safety are yet to be established. However, it should be noted that the supercapacitors generally exhibit unsatisfactory and much lower energy density than rechargeable batteries,[2] and thus extensive research efforts are devoted to increasing the energy density of supercapacitors. Practically, a combination of batteries and supercapacitors for balancing both energy and power densities is proposed to satisfy the demands where both high energy density and power density are needed.

Generally, the energy density of a supercapacitor is determined by both the electrode materials and the electrolyte. From the perspective of electrode materials, the most widely investigated electrode materials are carbon-based materials in which the charges are stored by the oppositely charged ion double layers formed at the electrode/electrolyte interface (known as electrical double-layer capacitors, EDLCs).[3] Owing to this intrinsic charge storage mechanism, the EDLC electrodes deliver low specific capacitances of generally 100−150 F g^{-1}.

Thus, the most widely adopted method now-a-days is to seek for electrode materials beyond carbon with rich redox reaction sites on/near the surface (known as pseudocapacitance), which will deliver much higher specific capacitance than carbon. Besides, battery-type electrodes also demonstrate much higher specific capacitance via diffusion-controlled redox reactions.[4] However, their capacitances are limited by the slow diffusion rate and moderate electrolyte penetration.

Electrolyte has also been identified as one of the key components of supercapacitors, and various kinds of electrolytes have been developed, including liquid electrolyte and solid/quasi-solid-state electrolyte (SSE).[5] The SSE (including gel electrolytes and inorganic solid-state electrolytes) can act as both an ionic conduction medium and separator, and thus one of the major advantages using SSE is the simplification of packaging and fabrication processes. The liquid electrolyte can further be divided into aqueous electrolyte and nonaqueous electrolyte, of which the aqueous one is the most widely adopted in the literature owing to its high ionic conductivity and excellent safety properties. However, it should also be pointed out that the aqueous electrolyte also delivers some significant disadvantages such as narrow voltage window. To solve this issue, a new

concept such as the water-in-salt is suggested which can expand the voltage window up to 3.0 V without water splitting.[6] Besides, it is generally supposed that the electrolyte should be electrochemically inert in which no redox reactions occur.[5] Inspired by the pseudocapacitive electrodes with rich redox reactions on/near the surface of electrodes that can provide additional capacitance, a growing number of researchers are beginning to pay attention to the redox electrolyte to achieve the enhanced specific capacitances.[7] For carbon electrodes, considering the various redox states of electrolyte additives and the redox transformation of electrolyte species, the capacitance of the full devices may be several times higher than that without redox additives in the electrolyte. If the pseudocapacitance or battery-type electrodes are used to replace carbon electrodes, the specific capacitances and corresponding energy densities of the devices can be further increased.[8] Regarding the calculation of overall energy density of super-capacitors including the mass of redox additive, the globally accepted standards are yet to be established. However, it should be pointed out that if the redox additive electrolyte serves as the ionic charge carriers, the total charge storage capability may depend on the formula mass of the redox species.[7] Albeit with the aforementioned advantages, the redox additives in the electrolyte often lead to the degradation of cycling stabilities as many redox electrolytes act as a shuttle, thus thwarting the very same purpose for which they have been added, which limit their practical applications.

Herein, in this mini-review, we will give a brief review on the classification, state-of-the-art progress, challenges, and prospects of the redox additives in the aqueous electrolyte.

CLASSIFICATION AND DEVELOPMENT OF REDOX ADDITIVES IN AQUEOUS ELECTROLYTE

Adding redox additives into the aqueous electrolyte has been proven to be an effective method to improve the electrochemical capacitive performance of supercapacitors besides the commonly used electrode-modifying method. The mechanism of energy storage with redox additive in aqueous electrolyte is pretty complex. Taking the carbon electrode for example, the general mechanism for electrochemical capacitance enhancement by the redox additive in the electrolyte can be schematically illustrated in Figure 1.[7] The total electrochemical reactions include the following processes: (i) the redox species
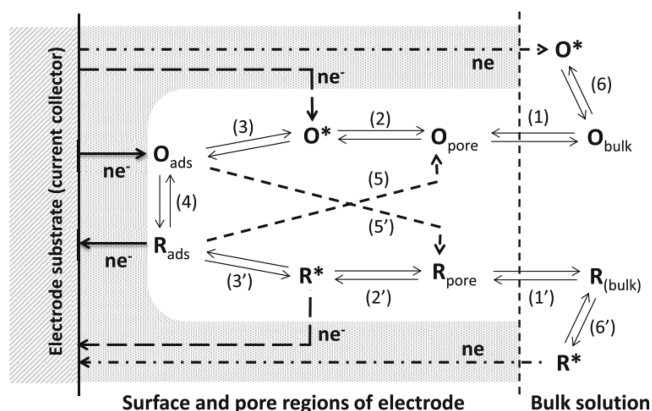

Figure 1. Illustration of charge storage mechanisms in the porous carbon electrode of a supercapacitor with a redox electrolyte. (Reproduced with permission from *J. Electrochem. Soc.* **2015**, *162* (5), A5054−A5059).[7]

(O and R for oxidized and reduced states) enter into the hydrophilic pore of the carbon electrode (processes 1 and 1′); (ii) the redox species reach transition states (O* or R*) (processes 2 and 2′); (ii) the transition states are converted to adsorbed states (O_{ads} and R_{ads}) (processes 3 and 3′); (iv) the electrons transfer between the adopted states (processes 4 and 4′); and (v) probably without invoking adsorption (processes 5 and 5′) in the bulk electrolyte. Generally speaking, the pore size distribution of the carbon electrode plays a vital role in the electrochemical energy storage performance. Taking aqueous electrolyte with iodide-based redox additive (the size of I^{3-} solvated by four water molecules is 1.8 nm) for example, it is regarded that the mesopore (2−50 nm) is the most adapted for the electrosorption process.[9]
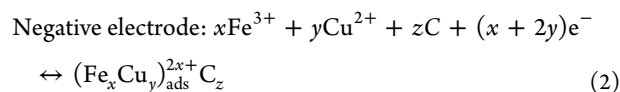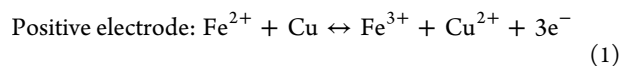
Several selection criteria should be considered for the practical applicability of redox additives in aqueous electrolyte. The standard redox potential is an important criterion which can guide the balancing of redox activities in the electrolytes and electrodes. Besides, the solubility in water, toxicity, safety, material cost, and environmental influence should also be considered.

Currently, for different aqueous electrolytes, various kinds of redox additives have been developed. According to their chemical compositions, the as-reported redox additives in aqueous electrolyte for supercapacitors can be generally divided into two catalogs: inorganic and organic redox additives. Based on the number of redox species, the redox additives can be catalogued to single and dual redox additives. Also, from the perspective of pH values, the redox additive can be classified into redox additives in acidic electrolyte, in alkaline electrolyte, and in neutral electrolyte, respectively. In the following parts, we will focus our discussion on the classification of inorganic and organic redox additives.

STATE-OF-THE-ART PROGRESS ON REDOX ADDITIVES IN AQUEOUS ELECTROLYTE

Inorganic Redox Additives in Aqueous Electrolyte. The first reported redox additive of aqueous electrolyte was proposed by Tanahashi et al. in 2005 by mixing the solution of 5.0 M H_2SO_4 (50.0 mL) and 1.0×10^{-1} M $AgNO_3$ (1.0 mL), which was inspired by the results that Cu-deposited activated carbon fiber cloth (ACFC) could make a contribution to the enhancement of capacitance via redox transition reactions.[10] Owing to the pseudocapacitance associated with the redox reaction of the Ag^+/Ag redox couple, the ACFC electrodes exhibit a maximum specific capacitance of 248 F g^{-1} which is 300% higher than that without the $AgNO_3$ additive. Later in 2007, Li et al. investigated the electrochemical behaviors of porous carbon electrode with the introduction of Cu^{2+} and Fe^{2+} into H_2SO_4 electrolyte, which delivered a significantly improved specific capacity of 223 mAh g^{-1} at a current density of 0.1 A g^{-1}.[11] The mechanism can be expressed as

$$\text{Positive electrode: } Fe^{2+} + Cu \leftrightarrow Fe^{3+} + Cu^{2+} + 3e^- \tag{1}$$

$$\text{Negative electrode: } xFe^{3+} + yCu^{2+} + zC + (x + 2y)e^-$$
$$\leftrightarrow (Fe_xCu_y)_{ads}^{2x+}C_z \tag{2}$$

These redox additives generally utilize the reversible conversions of metal ions at different valence states and are thus restricted to work only in acidic and neutral electrolytes, which cannot be
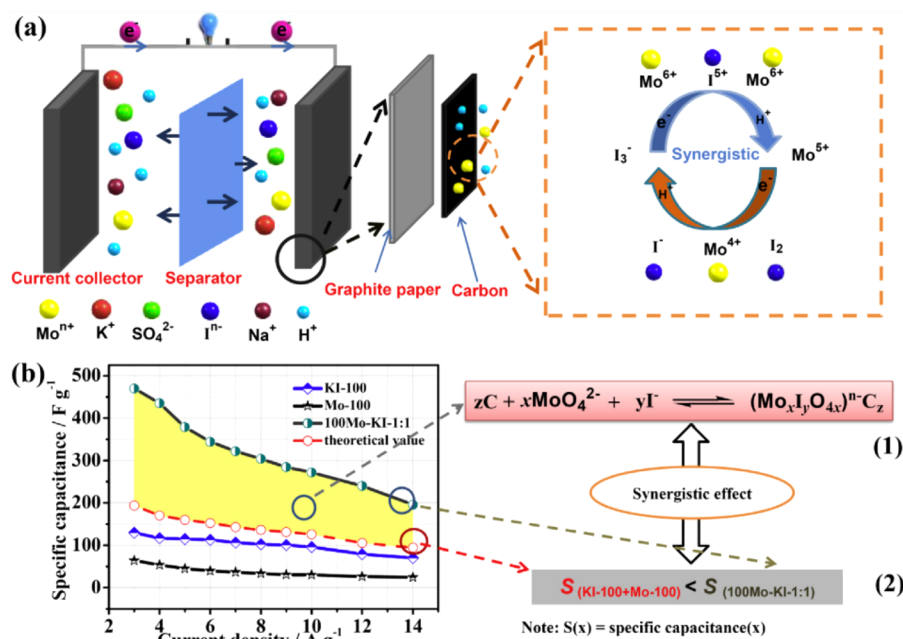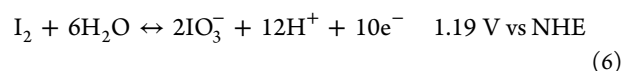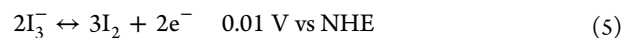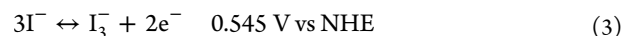
Figure 2. (a) Electrochemical reaction mechanism of the synergistic effect between Na_2MoO_4 and KI in the mixed electrolyte and (b) GCD curves at various current densities. (Reproduced with permission from *J. Power Sources* **2017**, *341*, 448−456).[13]

effectively applied in alkaline electrolyte together with the high performance pseudocapacitive and battery-type electrodes.

Different from the metal ion redox additives, Na_2MoO_4 is a typical redox additive which can work in various aqueous electrolytes. By adding 0.1 M Na_2MoO_4 into 1 M Li_2SO_4 solution, the specific capacitance of the AC//AC supercapacitor was increased to 121 F g^{-1} from 103 F g^{-1} in the voltage range of 1.6 V owing to the pseudofaradaic contribution. Moreover, the potentiostatic floating of the capacitor at 1.6 V could work stably for 120 h in the Li_2SO_4 + Na_2MoO_4 electrolyte. The Na_2MoO_4 additive has also been demonstrated to work effectively in acidic electrolyte. For instance, Sun et al.[12] investigated the electrochemical capacitive performance of N-doped porous carbon in 1 M H_2SO_4 electrolyte with the addition of different amounts of Na_2MoO_4. It was found that by tuning the amount of Na_2MoO_4 in the electrolyte a high gravimetric specific capacitance of 841 F g^{-1} was achieved at a high specific current of 15 A g^{-1}, which was 375.1% of that in pure H_2SO_4 electrolyte, and a high value of 440 F g^{-1} was still maintained at a much higher specific current of 35 A g^{-1}. Introducing another redox additive to construct dual redox additives with different potentials can simultaneously contribute to the enhanced energy storage capability. In this regard, Xu et al.[13] introduced KI into the Li_2SO_4 + Na_2MoO_4 electrolyte to form dual redox additives. For a nanoporous carbon electrode, by optimizing the molar ratio and concentration of redox additives as well as the voltage window of the device, the resultant specific capacitance enhancement of 17.3 times can be achieved compared to that without redox additive added in a two-electrode configuration. The increase of specific capacitance is attributed to the synergistic effect of Na_2MoO_4 and KI, as demonstrated in Figure 2. The faradaic capacitance resulting from the redox additive in the electrolyte is correlated with the chemical affinity between carbon materials and adsorbed ions, which might lead to the formation of complexes with substance of $(Mo_xI_yO_{4x})^{n-}C_z$ during the electrochemical reactions and thus promote the redox reactions of Mo^{n+} and I^{n-}

at the interface of the carbon electrode and electrolyte ions and edge site carbon atoms.

Except for acting as a coadditive in the electrolyte, KI has also been tested as an aqueous electrolyte salt for a supercapacitor with a carbon electrode and exhibits exceptionally high electrochemical performance.[14] Owing to the stable redox reactions resulting from the various oxidation states of iodine from −1 to +5, an extremely high specific capacitance of over 1840 F g^{-1} can be achieved which is several times higher than that in conventional H_2SO_4 electrolyte. The detailed mechanisms are described as follows:

$$3I^- \leftrightarrow I_3^- + 2e^- \quad 0.545 \text{ V vs NHE} \tag{3}$$

$$2I^- \leftrightarrow I_2 + 2e^- \quad 0.535 \text{ V vs NHE} \tag{4}$$

$$2I_3^- \leftrightarrow 3I_2 + 2e^- \quad 0.01 \text{ V vs NHE} \tag{5}$$

$$I_2 + 6H_2O \leftrightarrow 2IO_3^- + 12H^+ + 10e^- \quad 1.19 \text{ V vs NHE} \tag{6}$$

Inspired by the above-mentioned results, the same authors[9] further investigated the influence of alkali metal species (lithium, sodium, potassium, rubidium, and cesium iodides) on the electrochemical capacitive performances and found that among all these alkali metal iodides RbI exhibited the highest specific capacitance of 2272 F g^{-1}, while LiI displayed the lowest value of 300 F g^{-1}. The difference is caused by many factors such as ion/ion and ion/solvent interactions, ion mobility and polarizability, hydration effects, as well as faradaic reactions of iodide species. Additionally, KI has also been investigated as a single redox additive in acidic, alkaline, and neutral electrolytes, respectively. For instance, Wang et al.[15] reported the electrochemical capacitor with aqueous KI−KOH electrolyte, which demonstrated superior electrochemical performance with improved specific capacitance, lower self-discharge rate, and low-temperature stability compared with that with pure KOH electrolyte. Similar to the KI additive, KBr has also been found as an effective redox additive in aqueous electrolyte for supercapacitors. Tang

et al.[16] investigated the electrochemical capacitive properties of functioning carbon nanotube electrodes and discovered that the maximum energy density in 1 M Na_2SO_4 + 0.5 M KBr electrolyte was 4 times larger than that in 1 M Na_2SO_4 electrolyte. The enhanced performance is attributed to the Br^-/Br^{3-} conversion.

It is known that VO^{2+}/VO_2^+ species exhibit well reversible redox reactions at the electrode−electrolyte interface and are applied in vanadium redox flow batteries extensively. $VOSO_4$ as the source of VO^{2+} was thus introduced as a promising redox additive to evaluate the electrochemical performance. Very recently, Wang and co-workers[17] studied the electrochemical performance of vanadium oxide nanoribbons/3D-graphene composites (VO_x-3DG) in the aqueous electrolytes of KCl and $VOSO_4$ + KCl. They observed that both the capacitance and stability could be significantly improved in $VOSO_4$ + KCl electrolyte compared with those in KCl electrolyte. By optimizing the electrolyte, the capacitance of the VO_x-3DG electrode after 500 galvanostatic charge−discharge (GCD) cycles was 7.2 times higher than the initial value. The improvement is attributed to the dual role of $VOSO_4$ during the GCD process, namely, the capacitance increase by its redox reactions and the facilitation of vanadium oxide electro-deposition over the electrode surface.

Besides, the aforementioned inorganic redox additives, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, are the most widely used redox additives in aqueous electrolyte for supercapacitors and have attracted considerable attention in recent years. The first example of $K_3Fe(CN)_6$ as a redox additive was proposed by Su et al. in 2009.[18] By adding 0.1 M $K_3Fe(CN)_6$ into 1 M KOH as electrolyte and using Co−Al-layered double hydroxide (Co−Al LDH) synthesized via a homogeneous precipitation method as a battery-type electrode, an initial discharge specific capacitance of 712 F g^{-1} was obtained, while the value was only 226 F g^{-1} in pure KOH electrolyte. The high reversibility of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ ion pair at the electrode/electrolyte interface coupled with the redox transition of Co(II)/Co(III) in the Co−Al LDH electrode is believed to be the key factor to improve the electrochemical performance. As revealed by CV at a slow scan rate, the hexacyanoferrate (II) or (III) ions can interact with Co−Al LDH, and the hexacyanoferrate ions play the role of "electron shuttle" in the charge/discharge processes of the Co−Al LDH. The corresponding schematic illustration of the energy storage mechanism is shown in Figure 3. Furthermore, the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is also demonstrated to be able to work in neutral electrolyte. For instance, by combining laser-scribed AC with $K_3Fe(CN)_6$ in 1 M Na_2SO_4 electrolyte, the electrochemical capacitive performances were significantly improved. A specific capacitance of 364.6 mF cm^{-2} was delivered, which was 13 times higher than that using

nonscribed AC electrodes and acetonitrile-based electrolyte (28 mF cm^{-2}). As discussed above, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ can work as a redox additive in various electrolytes and is compatible with both EDLC electrode and battery-type electrode. Notably, constructing an asymmetric supercapacitor is regarded as an effective method to improve the energy density of the device. In this fashion, Nagaraju et al.[8] assembled an asymmetric supercapacitor with cauliflower-like nickel selenide nanostructures as a cathode and commercially available AC as an anode in the 1 M KOH + 0.02 M $K_3Fe(CN)_6$ electrolyte. The device exhibited a high energy density of 32.8 W h kg^{-1} at a power density of 677 W kg^{-1} and 98% capacity retention after 5000 cycles. The results successfully demonstrate the practical applicability of a $K_3Fe(CN)_6$ redox additive.

Organic Redox Additives in Aqueous Electrolyte. Compared with inorganic redox additives in the electrolyte, organic redox additives have also attracted considerable research attention owing to the structure diversity. Hydroquinone (HQ) is the first reported organic redox additive that can work effectively in acidic electrolyte.[19] By adding 0.38 M HQ into 1 M H_2SO_4 (HQ/H_2SO_4) as electrolyte, the specific capacitances of four different types of carbon electrodes were at least two times higher than those without HQ in electrolyte. Initially, the increase is attributed to the additional pseudocapacitive contribution arising from the quinone/HQ faradaic reactions. Further investigation[20] demonstrated that when constructing the hybrid AC//AC supercapacitors using the HQ/H_2SO_4 electrolyte the anode exhibited a battery-type behavior, while the cathode displayed a pseudocapacitive hydrogen electro-sorption process besides the conventional EDLC behavior. As a consequence, specific capacitances of 5017 F g^{-1} for the anode and 477 F g^{-1} for the cathode and high energy density of 30.6 Wh kg^{-1} could be achieved.

To further increase the electrochemical capacitive performance of HQ/H_2SO_4, several methods have been developed. One is introducing another suitable redox additive to form a dual redox electrolyte to create a tunable redox shuttle that controls the electron transfer processes. It has been recently reported[21] that adding Keggin-type phosphotungstate anions into HQ/H_2SO_4 gives rise to significantly increased specific capacity and energy density (40.3 mAh g^{-1} and 20.0 Wh kg^{-1}) compared with those using a single redox electrolyte (11.4 mAh g^{-1} and 4.1 Wh kg^{-1}). Another method is to modify the molecular structure of HQ. In this way, Gastola et al.[22] prepared the brominated hydroquinone, dibromodihydroxybenzene (2,5-dibromoben-zene-1,4-diol, HQBr), and investigated its electrochemical performance as a redox additive in KOH electrolyte. The introduction of bromine into the hydroquinones should change their physicochemical properties (conductivity, reactivity, mobility, etc.), and the density function calculations and experiments have confirmed these expectations. Consequently, when using the optimum HQBr and KOH contents in the electrolyte, the AC electrodes delivered a high specific capacitance of 314 F g^{-1}. The outstanding performance can be attributed to the complex redox activity of the hydroquinone/quinone couple and Br^- conversions, as demonstrated in Figure 4.

However, it should be noted that the above-mentioned organic redox additives are generally composed of small molecules with large HOMO−LUMO gap (HLG) and thus possess poor electronic conductivity which will finally result in the low power density of supercapacitors. To overcome the obstacles, Xiong and coauthors[23] designed an indole-based
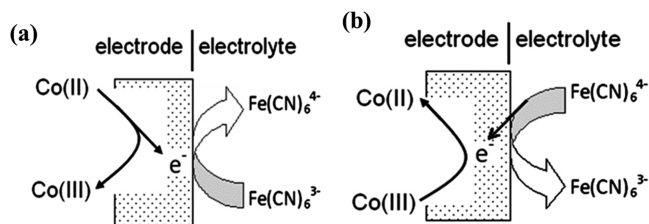

Figure 3. Illustration of the role of $K_3Fe(CN)_6$ in the courses of (a) charge and (b) discharge for the Co−Al LDH electrode. (Reproduced with permission from *Phys. Chem. Chem. Phys.* **2009**, *11*, 2195−2202).[18]
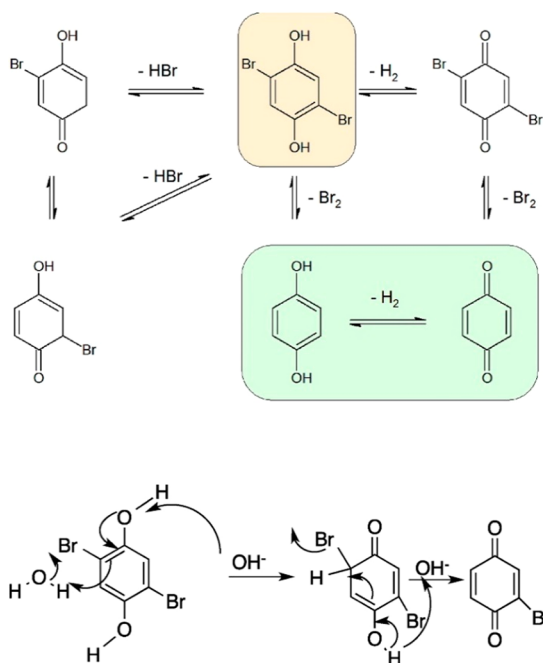
Figure 4. Several reaction pathways of 2,5-dibromobenzene-1,4-diol during supercapacitor operation. (Reproduced with permission from *J. Power Sources* **2016**, *326*, 587−594).[22]

conjugated macromolecule consisting of a 5,6-dihydroxyindole/5,6-quinoneindole motif as a redox additive in acidic electrolyte. When coupling the electrolyte with interconnected porous and honeycomb-like carbon electrodes, the supercapacitor delivered a high specific capacitance of 205 F g^{-1} at an ultrahigh current density of 1000 A g^{-1}. An energy density of 8.8 Wh kg^{-1} with the maximum power density of 153 kW kg^{-1} as well as excellent cycling stability over 20 000 cycles were achieved. These outstanding performances could be attributed to the lowered HLG (HLG of 5,6-dihydroxyindole/5,6-quinoneindole of ca. 5.0 eV, while 2.5 eV for the indole-based conjugated macromolecule containing 5,6-dihydroxyindole/5,6-quinoneindole motifs) and increased structural stability due to higher delocalization energy.

■ CONCLUSIONS AND PERSPECTIVES

In summary, introducing redox additives into aqueous electrolyte has been demonstrated to be an effective method to improve the electrochemical capacitive performance of supercapacitors. The classification and state-of-the-art progress of the redox additives in aqueous electrolyte for high performance supercapacitors are briefly discussed. The as-discussed redox additive in aqueous electrolyte and their electrochemical performances can be summarized in Table 1.

Despite the above-mentioned progresses of redox additives in aqueous electrolyte, several issues still remain and should be addressed to meet their practical applications. A common challenge for most of the redox additives is the redox shuttling effect which can cause a severe self-discharge process (SDP).[24] Suppressing the SDP is of great importance as it is closely related with the energy efficiency of supercapacitors. However, little attention has been paid to such issues. As pointed out by Chen et al.,[24] the primary reason for the fast SDP is the migration of redox electrolyte between two electrodes. It takes 11 524 s for supercapacitor voltage to decrease from 0.8 to 0.3 V (4.33 × 10^{-5} V/s) using the 1 M H$_2$SO$_4$ as electrolyte. However, the time decreases to only 1462 s (3.42 × 10^{-4} V/s) for the same voltage drop when using 0.4 M HQ + 1 M H$_2$SO$_4$ as electrolyte. Taking HQ as an example, as schematically shown in Figure 5,
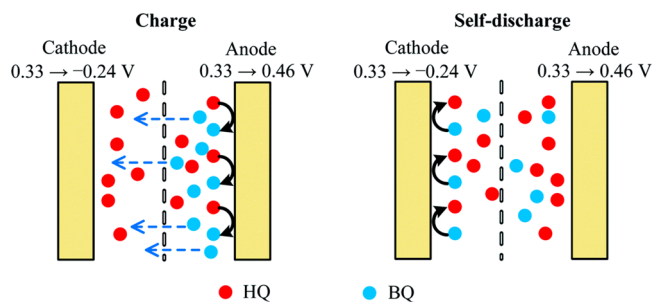

Figure 5. Schematic of the mechanism of charge and SDP of HQ-enhanced supercapacitor. (Reproduced with permission from *Energy Environ. Sci.* **2014**, *7* (5), 1750−1759).[24]

during the charge process, the HQ is transformed to BQ and adsorbed on the surface of the anode. After that, the obtained BQ diffuses to the cathode and is finally reduced to HQ, causing severe SDP. Considering the different mechanisms of redox additives, two strategies are suggested to suppress the redox shuttling effect: (1) using ion-exchange membrane to block the migration of the redox species and (2) choosing special redox additives that can be converted into insoluble species and deposited onto the electrode during the charge process.

Table 1. Summaries on the Redox Additive in Aqueous Electrolyte and Their Electrochemical Performances for Supercapacitors

electrode materials	electrolyte	redox species	performances	references
ACFC	H$_2$SO$_4$ + AgNO$_3$	Ag$^+$	248 F g^{-1}	10
porous carbon	H$_2$SO$_4$ + CuSO$_4$ + FeSO$_4$	Cu^{2+} and Fe^{2+}	223 mAh g^{-1}	11
AC	H$_2$SO$_4$ + Na$_2$MoO$_4$	MoO$_4^{2-}$	841 F g^{-1}	12
nanoporous carbon	Li$_2$SO$_4$ + KI + Na$_2$MoO$_4$	I$^-$ + MoO$_4^{2-}$	470 F g^{-1}	13
AC	KI	I$^-$	1840 F g^{-1}	14
carbon fibers	KI + KOH	I$^-$	251 F g^{-1}	15
functionalized CNT	Na$_2$SO$_4$ + 0.5 M KBr	Br$^-$	28.3 Wh kg^{-1} at 0.5 A g^{-1}	16
VO$_x$-3DG	VOSO$_4$ + KCl	VO^{2+}	8072 mF cm^{-2}	17
Co−Al LDH	K$_3$Fe(CN)$_6$ + KOH	Fe(CN)$_6^{3-}$	712 F g^{-1}	18
AC	HQ + H$_2$SO$_4$	HQ	5017 F g^{-1}	19
hierarchical porous carbon	H$_3$O$_{40}$PW$_{12}$ + HQ + H$_2$SO$_4$	H$_3$O$_{40}$PW$_{12}$ + HQ	40.3 mAh g^{-1}	21
AC	HQBr + KOH	HQ + Br$^-$	314 F g^{-1}	22
honeycomb-like carbon	H$_2$SO$_4$ + dopamine + dopamine chloride	indole-based conjugated macromolecule	205 F g^{-1}	23

Another challenge is the aging of the supercapacitors during the charge—discharge process. Platek et al.[25] investigated the aging mechanism of KI redox electrolyte and discovered that the test method, galvanostatic cycling, and potentiostatic floating could influence the aging process in different perspectives. The float test triggered the redox-based side reactions, while the cycle test changed the structure of the carbon electrode to accelerate the aging process. Besides, some other special challenge should be considered for a special redox additive such as a collector corrosive issue of the bromine-based redox additive.

Last but not least, some perspectives will be suggested. First, most of the redox additives are just tested by coupling with EDLC electrodes at the present. To further increase the energy density of the device, pseudocapacitive or battery-type electrodes should be a better choice. Second, although the aqueous electrolyte possesses higher ion conductivity than an organic or solid-state electrolyte, the narrow water-splitting window of 1.23 V will greatly hinder the improvement of energy density. Therefore, designing a redox additive that can extend the water-splitting window is of great importance. Third, from an environmental perspective, seeking for an environmentally friendly and low-cost redox additive will also show a huge development prospect. Fourth, for practical application, the redox additive with some special functions such as low- and high-temperature tolerance properties should be of particular concern.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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